Chapter 2

Probing the Chemistry of Ammonia at the Liquid/Vapor Interface: Base-Catalyzed Dissociation of a Cleavable Surfactant Studied by Field-Induced Droplet Ionization Mass Spectrometry

2.1 Abstract

The uptake of gaseous species into aqueous solutions is a central process in atmospheric chemistry that strongly influences the composition and processing of aerosol particles. Extensive research into the mechanism of uptake has revealed the complexity that often underlies this process. For example, the uptake of gas-phase ammonia at the liquid/vapor interface involves the interplay of accommodation, solvation, proton transfer, and diffusion. This study investigates the potential for changes in liquid properties near the liquid/vapor interface upon uptake of NH_3 to initiate base-catalyzed reactions selectively near a liquid surface. Droplets 2.5 µL in volume containing the pH-sensitive cleavable surfactant hexadecyl betaine (HDB) are exposed to gas-phase ammonia and sampled by field-induced droplet ionization mass spectrometry (FIDI-MS). Surfactant dissociation to yield hexadecanol and betaine in aqueous solutions or betaine methyl ester in solutions containing methanol is observed to occur without modulation of the bulk pH, suggesting that this process takes place selectively near the droplet surface. Sequential sampling experiments confirm that the reaction does not continue in the absence of gas-phase NH_3, providing further evidence that dissociation is not the result of changes in bulk solution pH. A model of NH_3 uptake coupled with reaction and diffusion indicates that transient

increases in pH may occur near the droplet surface, resulting in an increased rate of base-catalyzed dissociation in the interfacial region in comparison to bulk solution.

2.2 Introduction

The uptake of gaseous acids and bases at aqueous interfaces has received significant attention in both theoretical and experimental studies due to its importance in numerous atmospheric environments. These studies also provide insight into the fundamental properties and unique reactivity of the water/air interface, such as the acidity of the water surface[96-98] and the degree of solvation required for proton transfer reactions to occur.[99] Gas uptake at the water/air interface is hypothesized to proceed by the "critical cluster" model, in which surface accommodation is followed by the formation of a cluster of solvent molecules around the adsorbed species that facilitates its transfer into bulk solution.[20] For example, in the case of hydrochloric acid, a combination of theoretical and experimental studies has concluded that hydrolysis occurs at the interface or in the first few surface layers via the coordination of water molecules both above and below the hydrogen chloride molecule, resulting in efficient solvation of the ions and the formation of a stable ion pair.[49,99] Proton transfer to or from a base or acid generally occurs rapidly once the molecule is solvated, and this process occurs in concert with diffusion through the liquid to determine the time scale and spatial extent of pH change in solution.

The process of adsorption of gaseous ammonia (NH_3) at the water/air interface has been the subject of numerous studies, as NH_3 is the primary soluble base present in the earth's atmosphere. Studies employing SFG spectroscopy for the analysis of the structure of the interfacial region of ammonia-water solutions at high concentrations (mole fraction X_{NH_3}

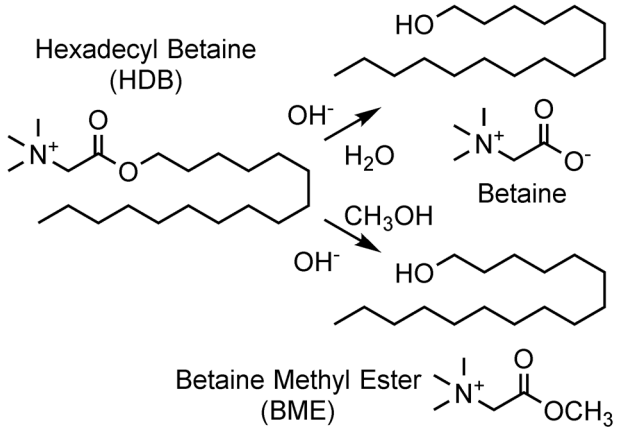
> 0.1) found that ammonia-water complexes are present in the interfacial region, with the nitrogen lone pair of ammonia interacting with the free OH groups present at the liquid/vapor interface.[100,101] Similarly, surface tension measurements of ammonia-water solutions with X_{NH_3} between 0.01 and 0.1 found the Gibb's energy of adsorption of NH_3 to the liquid surface was nearly twice that of the bulk free energy of solvation.[102] Study of the uptake of ammonia by aqueous solutions as a function of pH using DTFR experiments found a mass accommodation coefficient (the fraction of gas collisions with a surface that result in uptake) between 0.08 at 290 K and 0.35 at 260 K.[103] Evidence for the formation of a surface complex involving ammonia was also observed at high pH values. Intriguingly, a study of the pH of the water/air interface following exposure to gaseous NH_3 found a measureable increase in the local pH at the surface that was sustained for several minutes before equilibration with the bulk liquid.[49]

The properties of ammonia at the liquid/vapor interface have also been investigated extensively by theoretical methods, yielding significantly different results depending on the methods employed (e.g., including or excluding polarizability, molecular dynamics vs. embedded quantum mechanical methods). Several studies found a potential minimum for ammonia at the liquid/vapor interface ranging in magnitude from 2-8 kJ/mol,[104-106] whereas other calculations found no evidence of a potential minimum.[107,108] Simulations of ammonia-water solutions showed evidence that NH_3 is concentrated at the interface, whereas NH_4^+ is depleted in the interfacial region.[105,109,110]

Although the adsorption of ammonia at the water/air interface has been the subject of many investigations, further experimental studies are required to yield insight into the

intriguing behavior of this molecule in the interfacial region. In this study, we explore the potential of NH_3 uptake at the liquid/vapor interface to initiate base-catalyzed reactions of surface-active species. A solution containing a cleavable surfactant, hexadecyl betaine (HDB, Scheme 2.1), is analyzed by forming a quiescent droplet with a surfactant layer of HDB at the water/air interface, exposing it to NH_3 vapor, and sampling by FIDI-MS. These experiments indicate that the uptake of gaseous ammonia by a liquid surface leads to a localized increase in pH, inducing based-catalyzed reactions specifically at the liquid/vapor interface. A simple model of NH_3 uptake at the water/air interface in concert with reaction and diffusion within a droplet provides further evidence for an increase in pH near the droplet surface.

Scheme 2.1. Base-Catalyzed Dissociation of the Cleavable Surfactant Hexadecyl Betaine (HDB)



2.3 Materials and Methods

2.3.1 Materials

High-purity water was purchased from EMD Millipore (Billerica, MA). Ammonium acetate, concentrated ammonium hydroxide (28-30% by weight), and high-purity methanol

were obtained from J.T. Baker Avantor (Center Valley, PA). Hexadecyl betaine (2-(hexadecyloxy)-N,N,N-trimethyl-2-oxoethan-1-aminium chloride), dodecanoic acid, dodecyltrimethylammonium bromide (DTA), and ammonium bicarbonate were obtained from Sigma-Aldrich (St. Louis, MO) and used without further purification. New stock solutions of HDB were prepared daily at a concentration of 10 mM to prevent degradation. Stock solutions of 10 mM DTA and dodecanoic acid stored at −20° C and thawed for sample preparation. Hydrion short-range pH paper was obtained from Micro Essential Laboratory (Brooklyn, NY) to measure the pH of FIDI droplets following exposure to gaseous ammonia.

2.3.2 Field-Induced Droplet Ionization Mass Spectrometry (FIDI-MS)

Figure 2.1 shows the two experimental arrangements utilized for FIDI-MS experiments. The FIDI apparatus coupled to an LCQ mass spectrometer (Figure 2.1a) has been described in detail in a prior study,[83] and slight modifications to this design were implemented to couple the source to an LTQ-XL mass spectrometer (Thermo-Fisher, Waltham, MA), as shown in Figure 2.1b. In both designs, a droplet of ~1.6 mm in diameter (2.5 μL volume) is formed on the end of a 28-gauge stainless steel capillary by injection from an external syringe pump. This capillary is positioned equidistantly between two parallel plate electrodes separated by 6.3 mm. Following a 1 min delay period for droplet equilibration and formation of a surface surfactant layer, NH_3 vapor is leaked into the region via two gas inlets on either side of the droplet. The gas flow is maintained for a variable period of time up to 60 s, and the droplet is then subjected to a strong electric field by application of a high voltage to the back parallel plate electrode; the metal capillary on which the droplet

is hanging is also biased such that it is on an equipotential of the applied field. The strong electric field results in the ejection of highly charged, micron-sized progeny droplets,[85] which enter the atmospheric pressure inlet of the mass spectrometer and undergo evaporation and Rayleigh discharge to yield gas-phase ions in a manner similar to the mechanism of electrospray ionization.[111] The FIDI source designed for the LCQ (Figure 2.1a) employs a copper mesh as the high voltage electrode and the inlet of the mass spectrometer as the ground electrode. The FIDI source modified for use with the LTQ-XL (Figure 2.1b) utilizes two stainless steel plates mounted on ceramic rods (Kimball Physics, Wilton, NH) as the high voltage and ground electrodes. Experiments on droplets of 50/50% (v/v) methanol/water were performed with use of the LCQ, and those on purely aqueous droplets were performed with use of the LTQ. For each time point, at least four spectra were collected from separate droplets and averaged to give the presented time-resolved data. Following sampling by FIDI-MS, each droplet was collected on short-range pH paper (range 5.5-8.0, increments of 0.3 pH units), and the pH was determined by noting the change in color of the paper.

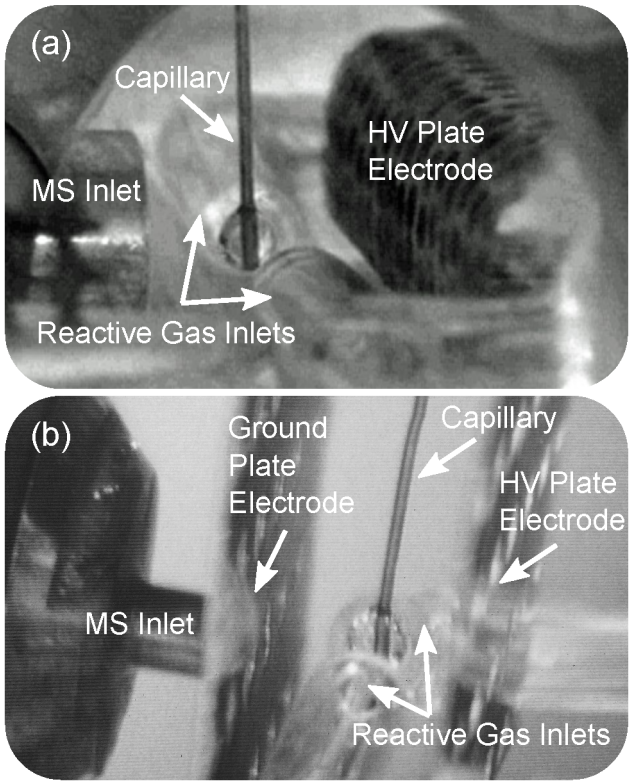


Figure 2.1. Experimental apparatus for monitoring interfacial reactions by FIDI-MS. Experiments performed with the LCQ mass spectrometer (a) utilized a copper mesh for the high voltage (HV) electrode and the MS inlet as a ground electrode, whereas experiments performed with the LTQ mass spectrometer (b) utilized stainless steel plates for the ground and HV electrodes.

2.3.3 Generation of Gaseous Ammonia

Two approaches were utilized to generate a flow of gaseous ammonia for droplet exposure. For experiments on droplets of 50/50% (v/v) methanol/water, a 32 mL/min flow of nitrogen was directed over the headspace above 3 mL of a ~150 mM ammonium hydroxide solution in the base of a U-shaped flow tube. For experiments on aqueous droplets, nitrogen gas was flowed through a fritted bubbler (64834-U, Sigma-Aldrich) containing 10 mL of 15 mM ammonium hydroxide at a rate of 50 mL/min. Gas flow rates were governed by a mass flow controller calibrated for nitrogen (πMFC, MKS Instruments,

Andover, MA). Flow rates and concentrations were optimized to ensure that the gas flow did not induce major changes in the bulk pH of droplets.

2.3.4 Sonic Spray Ionization

A sonic spray ionization (SSI) source was utilized in this work to study the kinetics of hydrolysis of HDB in buffered aqueous solution. The apparatus is constructed from a 1/16 in. tubing tee (Swagelok, Solon, OH) as described in detail in a previous study by Cooks and co-workers.[112] The source was operated with a nitrogen nebulizing gas flow rate of ~5 L/min and a sample infusion rate of 5 µL/min. An LTQ-XL was utilized for detection with the same instrumental parameters employed in FIDI-MS experiments to minimize differences in ion abundance between the two methods. Solutions of 100 µM HDB in either 50 mM ammonium bicarbonate or 25 mM ammonium acetate with pH adjusted by addition of acetic acid or ammonium hydroxide were prepared directly prior to analysis.

2.3.5 Model of NH_3 Uptake in Aqueous Solution

To better evaluate the interplay of uptake, diffusion, and reaction in these experiments, a simple model was developed to study the uptake of NH_3 vapor by aqueous droplets. The experimental system is modeled as a spherically symmetric droplet 1 mm in diameter. The Nernst-Planck diffusion model in the dimension r over time t is utilized to describe the movement of dissolved species in solution,[113-116]

$$\frac{\partial c_i}{\partial t} = r^{-2}\frac{\partial}{\partial r}\left[r^2\left(\sum_{k=1}^{N_s} D_{ik}\frac{\partial c_k}{\partial r}\right)\right] + j_i \qquad (2.1)$$

where c_i is the concentration of each species, N_s is the number of species, and j_i represents the rate of addition or depletion of a species via chemical reaction. The diffusion coefficient

of species i modified by the concentration gradient of other dissolved species k, represented by D_{ik}, is given by

$$D_{ik} = D_i \delta_{ik} - \frac{z_i z_k D_i D_k c_i}{\sum_{k=1}^{N_s} z_k^2 D_k c_k} \quad (2.2)$$

where D_i is the diffusion coefficient of species i, δ_{ik} is the Kronecker delta function, and z_i is the charge of species i. This model accounts for the influence of electrostatic interactions on diffusion in the droplet. The diffusion constants utilized for each species are detailed in Table B.1.

In each simulation, the proton transfer reactions of ammonia were modeled along with the reactions of dissolved carbon dioxide,

$$\mathrm{NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-} \quad (2.3)$$

$$\mathrm{NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O} \quad (2.4)$$

$$\mathrm{2\ H_2O \rightleftharpoons H_3O^+ + OH^-} \quad (2.5)$$

$$\mathrm{CO_2 + H_2O \rightleftharpoons H_2CO_3} \quad (2.6)$$

$$\mathrm{H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+} \quad (2.7)$$

$$\mathrm{HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O} \quad (2.8)$$

The rate constants for the forward and reverse reactions used in the model are listed in Table B.2.

The initial conditions of the simulation are calculated assuming a pure water droplet in equilibrium with 400 parts per million (ppm) gas-phase CO_2 and no dissolved NH_3, giving a uniform initial droplet pH of 5.6, as detailed in Table B.3. The system boundary conditions are modeled by[103,117]

$$\frac{\partial c_i(r=0)}{\partial r} = 0 \tag{2.9}$$

$$\frac{\partial c_i(r=0.5)}{\partial x} = \left(\frac{\alpha_i}{D_{i,\,\mathrm{H_2O}}\sqrt{2\pi M_i RT}}\right)\left(P_{i,g} - \frac{c_i(r=0.5)}{H_i}\right) \tag{2.10}$$

where α_i is the mass accommodation coefficient of species i, M_i is the molar mass, R is the gas constant, T is the temperature (K), $P_{i,g}$ is the gas-phase pressure (Pa), and H_i is the Henry's law constant (mol Pa^{-1} m^{-3}), as given in Table B.4. Physically, these conditions correspond to analyte uptake at the liquid surface that is a function of the diffusion constant in solution ($D_{i,\,\mathrm{H_2O}}$), the number of gas-phase molecules impinging upon the surface ($\sqrt{2\pi M_i RT}$),[20] the fraction of impinging molecules adsorbed by the solution (α_i), and the difference between the gas-phase analyte partial pressure ($P_{i,g}$) and the equilibrium vapor pressure above the solution ($c_i(r = 0.5)/H_i$). The gas-phase pressure of all species except NH_3 and CO_2 are assumed to be zero (i.e., $\partial c_i(r = 0.5)/\,\partial r = 0$). The effect of a gas-phase concentration gradient induced as a result of uptake into the liquid, the preference of molecules for the interfacial region, and the convective transport of analytes are not modeled in this simplified system. Calculations were performed using the *pdepe* function in the MATLAB programming environment (MathWorks, Natick, MA).

2.4 Results and Discussion

2.4.1 Kinetics of HDB Hydrolysis Monitored by SSI

As shown in Scheme 2.1, the ester bond of HDB hydrolyzes under basic conditions via nucleophilic attack at the carbonyl by a hydroxide ion to yield hexadecanol and betaine. In the presence of methanol, betaine methyl ester (BME) is also formed in high yield. To

assess the kinetics of HDB hydrolysis, the reaction in buffered aqueous solution was monitored at pH 7, 8, and 9 by sonic spray ionization (SSI), as shown in Figure 2.2. Although SSI does not yield quantitative ion intensities due to preferential ionization phenomena common in spray ionization techniques,[111] SSI can be utilized to qualitatively assess the hydrolysis kinetics of HDB. Little dissociation of HDB was observed at pH 7 after 40 minutes, whereas half-lives of approximately 22 and 2 minutes were determined at pH 8 and 9, respectively. Strong agreement was obtained between experiments utilizing 50 mM ammonium bicarbonate and 25 mM ammonium acetate as buffers. These results indicate a strong pH dependence for dissociation of betaine ester surfactants, in agreement with a prior study.[118]

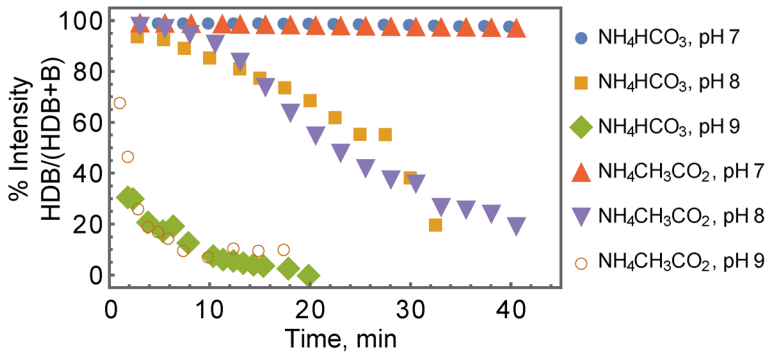


Figure 2.2. Dissociation of hexadecyl betaine (HDB) to betaine (B) at pH 7, 8, and 9. Plotted is the % intensity of HDB divided by the total intensity of betaine and HDB monitored by SSI-MS as a function of time. Solutions were prepared in either 50 mM NH_4HCO_3 or 25 mM $NH_4CH_3CO_2$ with pH adjustment by addition of acetic acid or ammonium hydroxide.

2.4.2 Investigation of NH_3-Catalyzed Reactions at the Water Surface

FIDI-MS studies of reaction at the liquid/vapor interface upon NH_3 uptake were performed in water alone and in water/methanol mixtures. Water/methanol (50/50% v/v) droplets of 2.5 µL in volume containing 100 µM HDB were exposed to a flow of gaseous NH_3 generated by a flow of nitrogen above a 150 mM NH_4OH solution at a rate of 32 mL/min for 0-60 s. Although the gas flow contains a significant concentration of NH_3, the flow is diluted upon exit from the reactive gas inlets, as the pull of air into the adjacent mass spectrometer inlet is approximately 1 L/min, resulting in a much higher flow of laboratory air in the vicinity of the droplet. Measurement of droplet pH following exposure to gaseous NH_3 using sensitive pH paper did not show a significant increase in the bulk pH of the droplets ($pH \leq 6.4$). Figure 2.3a shows the results of NH_3 exposure experiments for 50/50% (v/v) water/methanol droplets containing 100 µM HDB. Over the course of 60 s of exposure, the relative intensity of HDB is greatly reduced, and the product betaine methyl ester (BME) is observed with high intensity. The efficiency of this reaction without a significant change in the bulk pH suggests that this reaction occurs as a result of processes unique to the water/air interface.

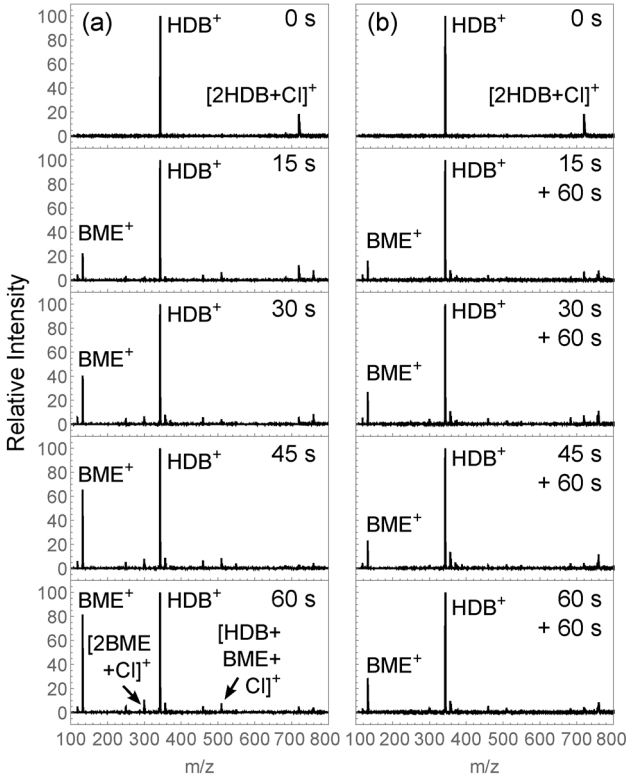


Figure 2.3. Exposure of aqueous HDB to ammonia vapors; (a) 100 μM HDB in 50/50 water/methanol is exposed to ammonia vapors at a flow rate of 32 mL/min; (b) 60 s after the initial FIDI sampling, each droplet is sampled a second time, and the results suggest diffusion of the product BME, significantly more hydrophilic than HDB, into solution.

If the dissociation of HDB occurs selectively at the liquid/vapor interface, then the reaction should cease in the absence of gaseous NH_3, and the BME product, which is hydrophilic and unlikely to localize to the droplet surface, should diffuse into solution until it reaches an equilibrium concentration throughout the droplet volume. Assuming that the diffusion coefficient of BME is similar to that of betaine ($\sim 1 \times 10^{-5}$ cm^2 s^{-1})[119], a substantial decrease in BME concentration near the liquid surface should be observed within 60 s in the case of an interfacial process. To probe this hypothesis, each droplet was sampled a second time by FIDI-MS following 60 s of equilibration with the reactive gas flow shut

off, yielding the spectra shown in Figure 2.3b. At short times (15-30 s of gas exposure), little difference in the intensity of BME is observed following the equilibration period. This result alone is significant, as it indicates that the reaction is not driven by a change in bulk pH, which would cause hydrolysis to continue in the absence of gaseous NH_3. At longer time points (45-60 s of gas exposure), there are clear differences in the relative abundance of BME. At these later exposure times, there is significantly more of the hydrolysis product BME at the interface, and the diffusion away from the surface is therefore more rapid and noticeable. Notably, the diffusion of products from the interface may be somewhat aided by the mixing of the droplet as a result of the first FIDI sampling, but the observation that BME does not increase in intensity following NH_3 exposure suggests the reaction occurs selectively near the droplet surface.

Dissociation of dissolved HDB upon exposure to gaseous NH_3 was also investigated in purely aqueous solution. Since hydrolysis of HDB produces hexadecanol (Scheme 2.1), which is highly insoluble in water, the concentration of HDB was reduced to 50 µM. Higher concentrations were observed to lead to loss of droplets from the capillary due to a decrease in surface tension, likely as a result of substantial concentrations of hexadecanol at the droplet surface. In addition, the zwitterionic betaine product generated in aqueous solution is challenging to detect by FIDI-MS, especially in comparison to the highly surface-active HDB parent ion, and the loss of HDB was therefore monitored with respect to the nonreactive dodecytrimethylammonium ion (DTA), added at a concentration of 7.5 µM. Dodecanoic acid was also added to the sample at a concentration of 100 µM to decrease the surface tension of the aqueous sample and therefore allow for FIDI-MS sampling.

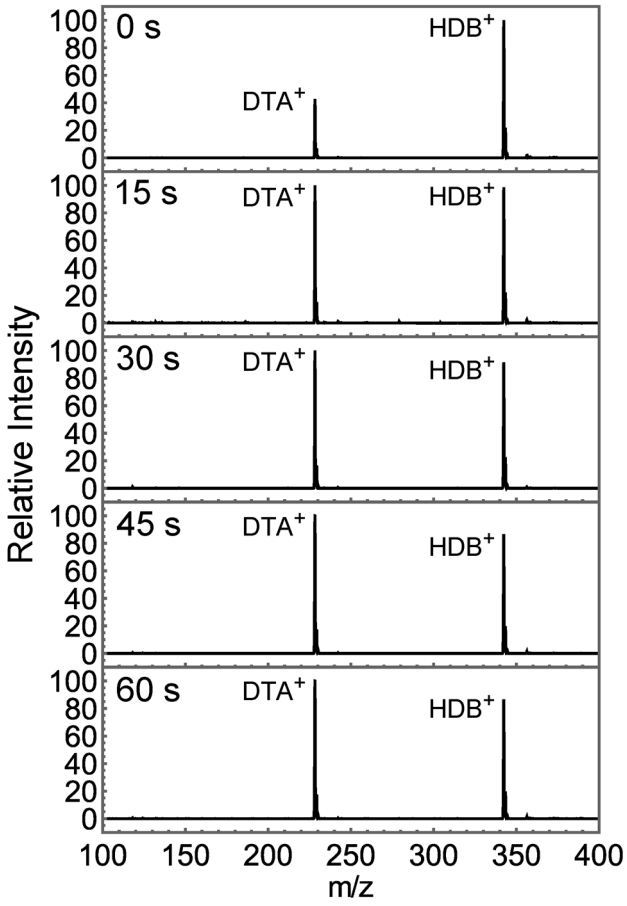


Figure 2.4. FIDI-MS of aqueous HDB solutions exposed to NH_3. Samples of 50 μM HDB, 100 μM DDA, and 7.5 μM DTA were exposed to gas-phase NH_3 generated by a flow of 50 mL/min of N_2 through a fritted bubbler containing 10 mL of 15 mM NH_4OH. The relative intensity of HDB with respect to DTA decreases rapidly in the first 15 s and then slowly thereafter.

The FIDI-MS spectra collected following the exposure of aqueous HDB to NH_3 are shown in Figure 2.4. Over the course of 60 s of exposure, the relative intensity of HDB with respect to DTA is found to decrease significantly, with the most substantial change occurring in the first 15 s of NH_3 exposure. The bulk pH of the droplet was also measured following each experiment and was not found to increase substantially ($pH \leq 6.4$). As in the water/methanol solutions, these results suggest that the dissociation of the surfactant at

the liquid/vapor interface is not initiated by a change in the bulk pH but rather by a base-catalyzed reaction specific to the interface.

2.4.3 Mechanism for an Enhanced Dissociation Rate at the Interface

A theoretical model of ammonia uptake coupled with diffusion and reaction in aqueous solution was developed to complement the experimental observations of base-catalyzed reactions at the liquid/vapor interface. The model accounts for the presence of dissolved carbonic acid in equilibrium with gas-phase CO_2 and monitors the concentration of analytes throughout a droplet of radius 0.5 mm following uptake of NH_3 at the water/air interface for 0-60 s. Shown in Figure 2.5 are the calculated pH values in solution for varying gas-phase concentrations of NH_3. At a gas-phase NH_3 concentration of 1×10^{10} molecules cm^{-3} (Figure 2.5a), an increase of pH from 5.6 to 6.7 near the surface of the droplet is calculated without a large change in the bulk pH of solution. This effect is even more pronounced for a gas-phase concentration of 1×10^{11} molecules cm^{-3} (Figure 2.5b), which yields an increase in surface pH to 7.6 compared to a bulk pH increase from 5.6 to 6.5. The pH near the surface remains above 7 throughout the 60 s modeling time. At higher concentrations of gas-phase NH_3 (1×10^{12} molecules cm^{-3}, Figure 2.5c), a large increase in the pH near the surface is also observed, but the pH in bulk solution is rapidly increased to greater than 7.

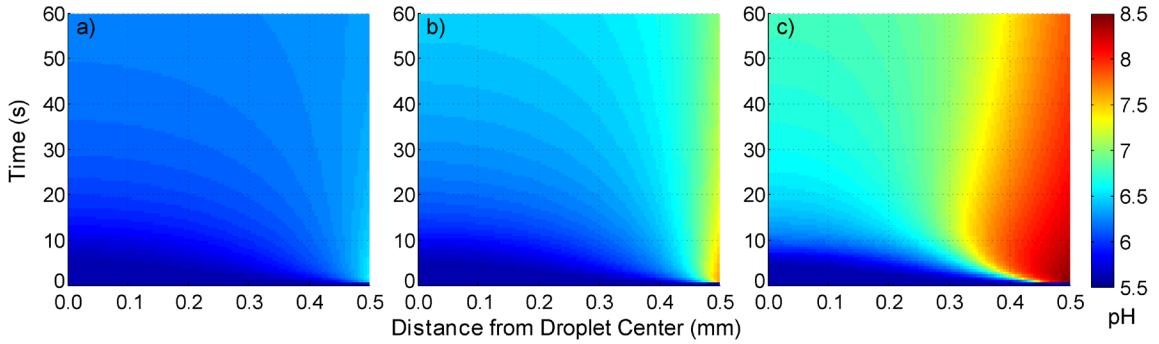


Figure 2.5. Modeling of uptake, reaction, and diffusion of ammonia within an aqueous droplet of 0.5 mm radius in equilibrium with gaseous carbon dioxide; plotted is the pH as a function of depth over sixty seconds of exposure to gas-phase NH_3 at a concentration of (a) 1×10^{10}, (b) 1×10^{11}, and (c) 1×10^{12} molecules cm^{-3}.

The modeled transient change in pH near the droplet surface occurs as a result of the difference between the reaction rate of ammonia with water to yield the hydroxide ion and the rate of conversion of dissolved carbon dioxide to carbonic acid, which acts as a buffer to maintain the initial pH of the solution. As NH_3 enters the liquid, it reacts quickly with water to increase the pH locally according to reactions 2.3 and 2.4 ($k_{2.3forward}$= 5.0×10^5 s^{-1}, $k_{2.4forward}$ = 4.3×10^{10} M^{-1} s^{-1}).[120,121] The depth at which this reaction occurs is limited by the diffusion rate of the ammonia within the droplet. As the concentration of the hydroxide ion increases, the rate of reaction between the bicarbonate and hydroxide ions also increases, regulating the increase in pH by reaction 2.8. The bicarbonate is quickly replenished by the reaction of carbonic acid with water (reaction 2.7). However, once the carbonic acid is depleted, the local buffering capacity of the liquid is limited by the rate of conversion of dissolved carbon dioxide to carbonic acid (reaction 2.6), a significantly slower process ($k_{2.6forward}$ = 0.04 s^{-1}).[122] Eventually, the concentrations of CO_2 (aq) and dissolved carbonic acid reach equilibrium once again, resulting in a buffering effect that

prevents a significant increase in droplet pH at the equilibrium concentration of dissolved NH_3. Nevertheless, an interfacial pH increase is still observed due to the transient increase in hydroxide ion concentration that occurs much more quickly than the replenishment of the buffering species. This result supports the experimental observation that dissociation of a base-cleavable surfactant can be achieved in an aqueous droplet without an increase in bulk pH.

The increase in dissociation of HDB detected experimentally may also be the result of processes occurring at the droplet surface by the formation of an ammonia surface complex. Ammonia is known to be enriched in concentration at the water/air interface in comparison to bulk solution at high concentrations.[100,101] Donaldson experimentally measured the Gibb's energy of adsorption to the surface to be −19.1 kJ/mol, as compared to a bulk free energy of solvation of −10.1 kJ/mol.[102] Shi and co-workers also found kinetic evidence for the formation of a surface complex of NH_3 during uptake from the gas phase, although such complexes were only observed at high pH.[103] A study by Clifford and Donaldson observed that the pH at the surface of liquid water exposed to gas-phase NH_3 could exist in disequilibrium with bulk solution for several minutes, but the differential was only on the order of 0.1 pH units.[49] However, a similar phenomenon may be present in these experiments, resulting in an increased rate of dissociation at the surface.

2.5 Conclusions

The process of uptake of NH_3 at the water/air interface has been investigated in depth previously by both theoretical and experimental studies. These studies have greatly enhanced the current understanding of the uptake process, establishing that uptake

proceeds by critical cluster formation,[63,102] indicating the presence of a thermodynamic minimum at the interface,[102] and constraining the mass accommodation coefficient.[103,123] However, further investigation is necessary to fully comprehend the complex interplay of adsorption, diffusion, and proton transfer reactions occurring in the interfacial region. This study utilizes the model system of a base-cleavable surfactant enriched in concentration at a liquid surface to demonstrate that base-catalyzed reactions can occur specifically at the liquid/vapor interface as a result of exposure to NH_3. Such reactions are observed to occur on droplet surfaces without significant modulation of the bulk solution pH, and multi-sampling FIDI-MS experiments suggest that the reactions do not continue upon cessation of base exposure, supporting the assertion that these reactions occur specifically in the interfacial region. A simple model of uptake coupled with diffusion suggests that a transient increase in pH near the liquid surface can occur upon exposure to gas-phase NH_3. A similar phenomenon has also been observed previously by Clifford and Donaldson.[49] Additional experimental and theoretical studies are required to fully elucidate the process of interfacial uptake, but these results demonstrate the ability of FIDI-MS to investigate novel processes occurring at interfaces that may have otherwise been inaccessible.